

## PROCESS TO MANUFACTURE NONVOLATILE MOS MEMORY DEVICE

### FIELD OF THE INVENTION

The invention relates to the general field of microelectronics with particular reference to nonvolatile MOS devices, more specifically to their manufacture.

### BACKGROUND OF THE INVENTION

In the upcoming age of nanotechnology, where devices may be a thousand times smaller than the microchips of today, semiconductor nanocrystals (Quantum Dots) have exhibited charge storage capability. This promises to be useful in future non-volatile memory applications and is currently under investigation by various research groups.

Charge storage devices that exceed the performance limits of a conventional floating-gate device have attracted a great deal of interest and are spurring rapid progress in this area. Quasi-nonvolatile MOS memory devices employing silicon nanocrystal charge-storage sites produced by ion implantation into the gate oxide have already been demonstrated (Tiwari et al., Appl. Phys. Lett. 68 (10), p.1377,1996) or germanium (King

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et al. IEDM Tech. Dig., 1998, p.115). Devices with embedded silicon or germanium nanocrystals, fabricated using ion implantation, exhibited superior data-retention characteristics as compared with conventional floating-gate devices. However, the ion implantation technique has its limitations such as a long processing time, a non-uniform germanium profile in the oxide and a compromise on the control oxide and interface quality. In addition, ion implantation places a lower limit on the top control-oxide thickness.

It has been suggested to use radio-frequency co-sputtering and rapid thermal annealing to form the oxide layer containing germanium nanocrystals (docket number CS01-074, serial number \_\_\_\_\_, file date \_\_\_\_\_, assigned to a common assignee as the instant invention). A high quality layer of thin tunnel oxide is first grown by rapid thermal oxidation prior to the sputtering process. However, the subsequent sputtering step results in a non-stoichiometric oxide film and also has a problem with particle generation.

A routine search of the prior art was performed with the following references of interest being found:

In US 6,128,243 Chan et al. show a memory for a SRAM using germanium Nanocrystals. US 5,783,498 (Dotta) shows a process to form germanium Nanocrystals. Sugiyama et al. show a memory device using germanium Nanocrystals in US 6,060,743

while, in US 6,090,666, Ueda et al. show another memory device using germanium Nanocrystals.

## SUMMARY OF THE INVENTION

It has been an object of at least one embodiment of the present invention to provide a process for manufacturing a non-volatile memory device.

Another object of at least one embodiment of the present invention has been that said device be of the MOS type.

Still another object of at least one embodiment of the present invention has been that the gate insulation of said device include germanium nanocrystals suspended in silicon oxide.

A further object of at least one embodiment of the present invention has been that formation of said gate insulation layer not require use of either RF sputtering or ion implantation.

These objects have been achieved by initial use of rapid thermal oxidation to grow a high quality layer of thin tunnel oxide. Chemical vapor deposition is then carried out to deposit a germanium doped oxide layer. A capping oxide is then deposited following which the structure is rapid thermally annealed to synthesize the germanium nanocrystals. The use of chemical vapor deposition process does not place a lower limit on the top control-oxide thickness. It also gives rise to better control oxide and interface quality as ion implantation damage is absent. In addition, the oxide in which the germanium nanocrystals are embedded is of better quality as compared to a sputtered oxide. This results in superior charge retention capability.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows formation of a layer of tunneling oxide on the surface of a silicon body.

FIG. 2 shows formation of a germanium doped oxide layer on FIG. 1.

FIG. 3 shows deposition of the capping layer.

FIG. 4 illustrates the appearance of the Ge nanocrystals after RTA.

FIG. 5 illustrates a finished device.

FIG. 6 is a C-V curve for a gate insulation layer of the type used in the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Overview: Rapid thermal oxidation is first used to grow a high quality layer of thin tunnel oxide. Chemical vapor deposition is then carried out to deposit a germanium doped oxide layer. A capping oxide is then deposited following which the structure is rapid thermally annealed to synthesize the germanium nanocrystals.

Referring now to FIG. 1, the process of the present invention begins with the provision of silicon body 11. Body 11 is preferably P-type but this is not essential for the invention to work. Tunnel oxide layer 12 is then grown on the upper surface of 11. This

was achieved by means of rapid thermal oxidation (at between about 900 and 1,000 °C for between about 5 and 60 seconds in a dry oxygen ambient), leading to an oxide thickness that is between about and 2 and 5 nm.

Next, as seen in FIG. 2, layer 21 of germanium doped silicon dioxide is deposited onto tunnel oxide layer 12. Layer 21 was formed by reacting silane in a mixture containing between about 5 and 30% germane and an oxygen source (such as ozone or nitrous oxide under conditions of low pressure chemical vapor deposition or plasma-enhanced chemical vapor deposition).

This is followed by the deposition of capping layer 31 (usually, but not necessarily, silicon oxide or silicon nitride) onto layer 21, as shown in FIG. 3. This layer is between about 10 and 50 nm thick and its deposition is achieved by using low pressure chemical vapor deposition or plasma-enhanced chemical vapor deposition.

At this point, formation of the charge retaining portion of the structure has been completed except for the formation of the germanium nanocrystals (see below). To complete formation of the nonvolatile memory structure, layers 12, 21, and 31 are patterned to form gate pedestal 52 as shown in FIG. 5. Then, using this gate pedestal as a mask, source and drain regions 51 that abut it (and extend downwards from it) are formed by ion implantation or by diffusing suitable dopant material through a hard mask.

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If the preferred version of P-type was used for the silicon body 11, then regions 51 will necessarily be N-type. Using conventional methods, electrical contacts to the source and drain regions and to the gate pedestal are made.

The final process step (after source and drain regions have been formed) is to subject the device to a rapid thermal anneal (between about 800 and 1,000°C for up to 300 seconds) in a non reactive gas such as argon or nitrogen. This precipitates some of the germanium out of solution in the form of nanocrystals having a mean diameter between about 2 and 10 nm, such as 41 in FIG. 5. Additionally, this annealing step serves to repair ion implantation damage as well as to activate dopant sites in the source and drain regions.

FIG. 6 is an example of a capacitance vs. voltage (C-V) curve for a device for a device having a similar structure to that described above (germanium nanocrystals embedded in an amorphous oxide) but with the germanium and capping oxide layers fabricated using sputtering (as in docket number CS01-074, serial number \_\_\_\_\_, file date \_\_\_\_\_, assigned to a common assignee as the instant invention). The counter-clockwise hysteresis seen in the C-V curve reflects the ability of the device to store charge.

When the applied voltage on the capacitor structure is increased from -15 to +15 volts, in steps of 0.5 volts, the capacitance follows curve 61 as the P-doped silicon at the silicon-oxide interface is driven from accumulation to inversion. When the silicon is in inversion, electrons will be injected into the gate oxide and subsequently be trapped at defect sites in, or at, the surface of the germanium nanocrystals. Consequently, as the applied voltage is swept, from +15 to -15 volts, in steps of 0.5 volts, the capacitance follows curve 62, resulting in a positive flatband voltage shift due to the electrons trapped by the Ge nanocrystals. Hence a counter-clockwise hysteresis is observed in the C-V characteristics.

What is claimed is: